

Rapid Synthesis of Magnetic Microspheres Poly(Glycidyl Methacrylate-co-Styrene) by Photopolymerization

(Kaedah Pantas untuk Sintesis Mikrosfera Poli(Glisidil Metakrilat-ko-Stirena)

Bermagnet melalui Fotopempolimeran)

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ABSTRACT

Three compositions of glycidyl methacrylate and styrene were added with Fe_3O_4 , ethylene glycol dimethacrylate (EGDMA), poly vinyl alcohol (PVA) and 2, 2-dimethoxy-2-phenylacetophenone (DMPP). Fe_3O_4 were dispersed within monomers and were exposed to the ultraviolet radiation for polymerization process. The Fe_3O_4 particles were introduced to enhance physical and chemical properties of the polymers. The thermal properties of polymer were improved after addition of styrene and Fe_3O_4 . Vibrating sample magnetometer (VSM) also exhibits copolymer with soft ferromagnetic properties. Field emission scanning electron microscopy (FESEM) showed the size of magnetic polymer microspheres were from 0.5 to 1.5 μm . The rough surface was also observed due to the presence of styrene.

Keywords: Fe_3O_4 ; glycidyl methacrylate; photopolymerization; styrene; thermal properties

ABSTRAK

Tiga komposisi glisidil metakrilat dan stirena ditambah dengan Fe_3O_4 , etilena glikol dimetakrilat (EGDMA), poli vinil alkohol (PVA) dan 2,2-dimetoksi-2-fenilasetofenon (DMPP). Fe_3O_4 disembarkan di dalam monomer dan didedahkan kepada sinaran ultra lembayung untuk proses pempolimeran. Zarah Fe_3O_4 dimasukkan untuk meningkatkan sifat fizik dan kimia polimer. Sifat terma polimer meningkat selepas penambahan stirena dan Fe_3O_4 . Magnetometer sampel bergetar (VSM) juga mempamerkan kopolimer bersifat ferromagnet lembut. Mikroskop elektron imbasan pancaran medan (FESEM) menunjukkan saiz mikrosfera polimer bermagnet ialah daripada 0.5 hingga 1.5 μm . Permukaan kasar juga diperhatikan kerana kehadiran stirena.

Kata kunci: Fe_3O_4 ; fotopempolimeran; glisidil metakrilat; sifat terma; stirena

INTRODUCTION

Magnetic polymer microspheres are widely applied in magnetic bio-separation, functioning as carriers for enzyme immobilization, cell isolation and protein purification (Chung et al. 2007). Biodegradable magnetic carriers have attracted increasing interest in biomedical and clinical research (Varma et al. 2011) due to their functional performance as an isolator of biological compounds (proteins, nucleic acids) and the separation of toxic and radioactive metals from complex mixtures (Horak et al. 2009).

Glycidyl methacrylate (GMA) based copolymers have received more attention due to their versatile applications (Iqbal et al. 2009) and they are only commercially available vinyl monomer carrying oxirane or epoxide group. Epoxy group has a unique reaction capability. They undergo ring opening when reacting with substances possess hydroxyl, amine or activated methylene groups. For these reasons, polymers with epoxide groups offer numerous functionalization possibilities in mild reaction conditions (Senkal et al. 2007). Microspheres copolymer beads based on GMA and ethylene glycol dimethacrylate (EGDMA), a type of copolymer that contains epoxy group which is

useful for polymer matrix modification. The produced copolymer can be utilized as matrix for enzyme attachment. The epoxy group is also easily to react with various reagents (Kuroda & Osawa 1995). Styrene, acts as a second monomer, can also enhance the rigidity of the copolymer (Chen & Lee 2001). The most common methods to prepare the copolymer include the dispersion polymerization (Chung et al. 2007), suspension polymerization (Horak et al. 2009), bulk polymerization, atom transfer radical polymerization (ATRP) and radical emulsion polymerization (Nita et al. 2008).

The conventional methods for preparing magnetic polymer microspheres can be divided into three classes: the magnetic materials are encapsulated by polymer coating; the magnetic materials are evenly dispersed within the polymer matrix after polymerization and the magnetic materials are filled in the pores of the pre-made polymer (Chung et al. 2007). In this study, the magnetic materials were dispersed within both monomers and were exposed to the UV light for polymerization process. The Fe_3O_4 particles were introduced to enhance physical and chemical properties of the copolymers. The objective of this work was to propose a rapid synthesis method for poly(glycidyl

methacrylate) and poly(glycidyl methacrylate-co-styrene). This study offered a rather straightforward and simple method by using suspension photopolymerization. The polymer and copolymers obtained were physically and thermally characterized.

EXPERIMENTAL DETAILS

MATERIALS

The following chemicals were obtained from commercial sources: glycidyl methacrylate, GMA (Sigma-Aldrich), styrene (Sigma-Aldrich), ethylene glycol dimethacrylate (EGDMA) (Sigma-Aldrich), polyvinyl alcohol, PVA, 2, 2-dimethoxy-2-phenylacetophenone, DMPP (Sigma-Aldrich) and iron oxide, Fe_3O_4 <50 nm (Sigma-Aldrich). Deionized water was used for making the aqueous phase during the experiment. All the purities were 99%.

PREPARATION OF MAGNETIC MICROSPHERES POLY(GLYCIDYL METHACRYLATE-CO-STYRENE)

Poly(GMA-co-styrene) was prepared by photopolymerization method. About 90% v/v of GMA was added to 5 mL of 1% w/v PVA and 60 μL EGDMA in a vial followed by 10% v/v of styrene. Then, 1.6% w/v DMPP and 0.1% w/v Fe_3O_4 was added in the mixture. This mixture was well dispersed by sonication procedure for 10 min. The mixture was then exposed to UV light source for 10 min and purged with nitrogen (Hanifah et al. 2009). Finally, the precipitate was collected by centrifugation. Deionized water was used to wash the collected precipitate. The precipitate was dried for 1 day to obtain magnetic microspheres copolymer. All the steps were repeated to get three different compositions of monomers and Fe_3O_4 .

CHARACTERIZATION METHODS

The detection of functional groups for the produced magnetic poly(GMA) and poly(GMA-co-styrene) was performed by Perkin Elmer spectrum BX FTIR spectrometer in nitrogen gas environment in the range of 4000-400 cm^{-1} .

The crystallite size of the magnetic cores of the microspheres was determined using the D8-advance bruker AXS powder diffractometer. The scans were conducted in the 2θ range from 3 to 80°. The average crystallite sizes were calculated by Scherrer's equation that was obtained during the analysis. The degradation temperatures for all samples were measured by Mettler Toledo STGA/SDTA 851. The samples were heated from room temperature to 600°C at a heating rate of 10°C/min under nitrogen flow 10 mL/min.

The morphology, shape and size of the microspheres magnetic copolymer were directly observed using a field emission scanning electron microscope (FESEM) zeiss supra 55VP. Prior to the examination, samples were coated with a thin layer of gold. The magnetic properties were measured using vibrating sample magnetometer (VSM) Lakeshore 7404 at room temperature. The sample of approximately of 20 mg was vibrated vertically and the dipole field of the sample induces an AC signal proportional to the magnetization of the sample in a pair of coils.

RESULTS AND DISCUSSION

The FT-IR spectra of the magnetic poly (GMA) and poly(GMA-co-styrene) are shown in Figure 1. The spectra confirmed the presence of the functional groups in poly (GMA) containing 0.2% Fe_3O_4 and poly(GS82) containing 0.2% Fe_3O_4 (as shown in the chemical reaction in Figure

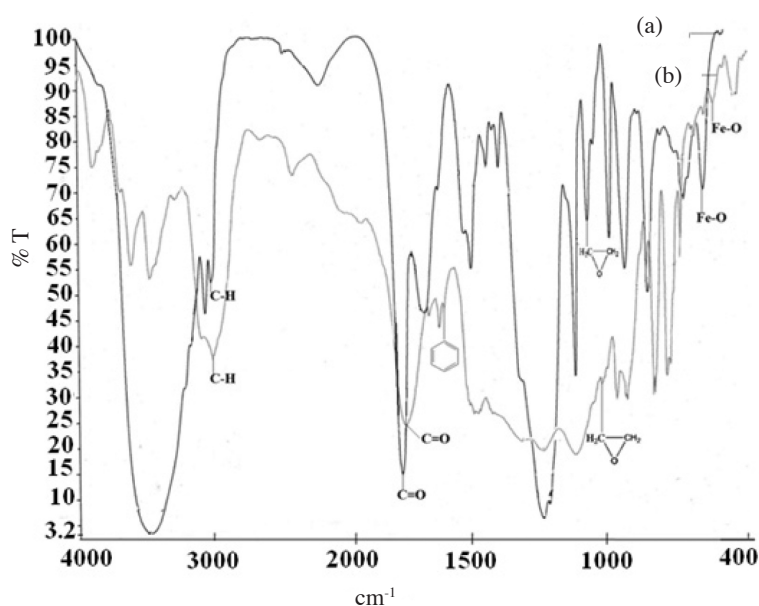


FIGURE 1. FT-IR spectra for (a) poly(GMA) containing 0.2% Fe_3O_4 and (b) poly(GS82) containing 0.2% Fe_3O_4

2). Carbon atom from GMA was attached to the carbon atom from styrene and formed the aliphatic carbons in the main chain and side chain of the copolymer (Brar & Yadav 2003). According to Pavia et al. (2009), the absorption peak at 1465 cm^{-1} is corresponding to the vibration of the $-\text{CH}_2$ group which is consistent with this finding. The absorption peak at 1598 cm^{-1} of aromatic $\text{C}=\text{C}$ group from styrene is also visible in the spectra. A new absorption peak was found in the FTIR spectra for poly(GMA-co-styrene) indicated that the $\text{C}=\text{C}$ group from styrene was attached with GMA. The shift of absorption peaks from 1729 cm^{-1} to 1725 cm^{-1} corresponding to the vibration of the carbonyl group proved the existence of poly(GMA-co-styrene). In addition, it was reported that the characteristic absorption peak of the $\text{Fe}-\text{O}$ bond of bulk Fe_3O_4 was at 570 cm^{-1} (Shamim et al. 2007) and has shifted to 536 and 539 cm^{-1} for poly (GMA) and poly(GS82) containing $20\% \text{ Fe}_3\text{O}_4$, respectively.

The XRD diffraction patterns of the microspheres beads showed the typical spectra for all the synthesized poly (GMA) and poly (GMA-co-styrene) containing Fe_3O_4 (Figure 3). This indicated that poly GS82 possessed the highest crystallite size which is 89.9 \AA , while for poly (GMA) is 83.4 \AA . This result showed that the crystallinity of the copolymer was increased after the addition of styrene. In addition, the presence of Fe_3O_4 has also enhanced the crystallinity of the copolymers. The crystallite size of GS91 showed the highest value, 104.5 \AA after adding $0.1\% \text{ Fe}_3\text{O}_4$. The X-ray diffraction patterns are shown in Figure 4. These results confirmed the presence of Fe_3O_4 particles in the prepared polymer microspheres by suspension photopolymerization. When the composition of Fe_3O_4 increased, the intensity of the peak also increased, indicating the amount of Fe_3O_4 did not affect the structure of the polymer chain.

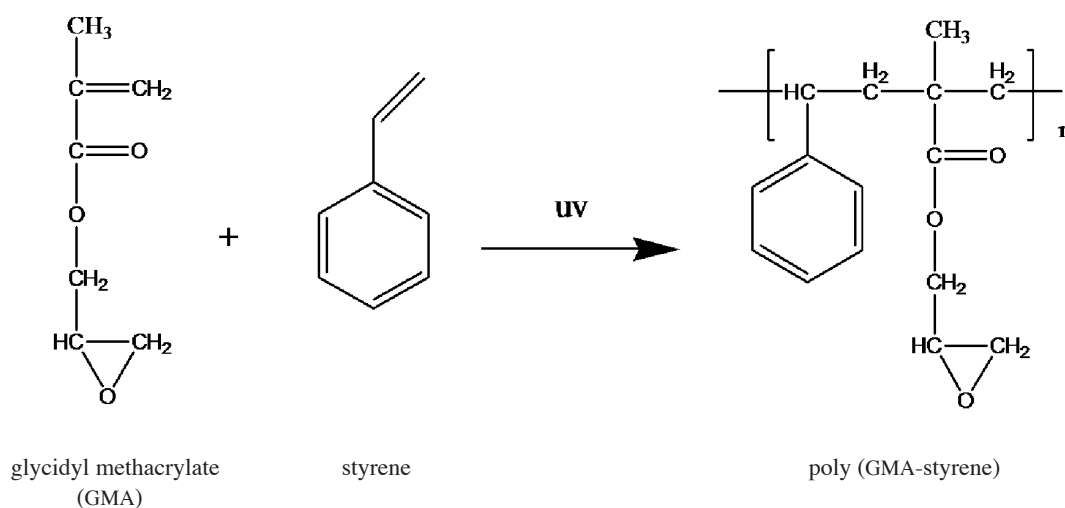


FIGURE 2. Reaction of glycidyl methacrylate and styrene using photopolymerization

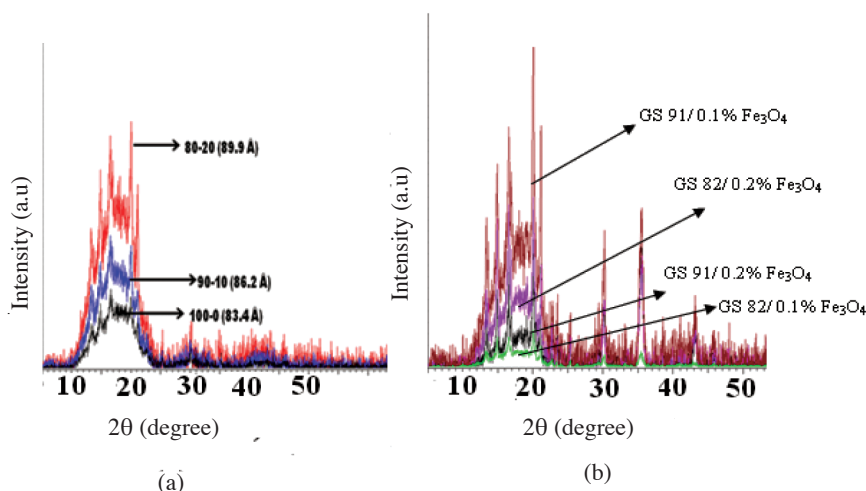


FIGURE 3. XRD analysis a) crystallite size for different copolymers and b) the crystallite size after different compositions of Fe_3O_4 has been added to the copolymers

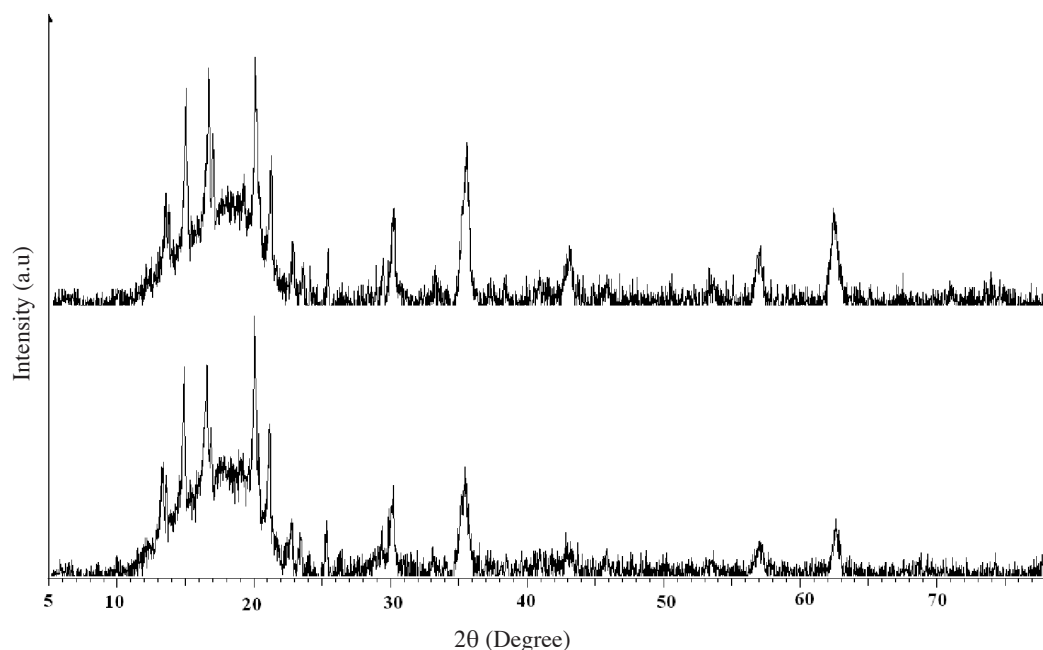


FIGURE 4. The effect of Fe_3O_4 compositions to the crystallinity of poly(GS82) θ

Figure 5 shows the thermograms for poly (GMA), GS91 and GS82. It can be seen that poly (GMA) undergoes one step of weight loss, of 19% between 140 and 450°C. The result can be explained as the loss of H_2O and CO_2 , due to the breakdown of weak linkages in backbone pendant group and thereby, volatilization of low molecular weight species (Vijayanand et al. 2007). The copolymers have typical pattern of thermograms, involved two steps of weight loss from 25°C to 600°C. The first weight loss for GS91 was observed from 130°C to 210°C and for GS82 from 130°C to 230°C with 3% weight loss. The second weight loss for GS91 and GS82 occurred at the same temperature from 350°C with 5% and 8% weight

of copolymers, respectively, due to the loss of benzene ring by breakage of main chains and volatilization of the cleaved products (Vijayanand et al. 2007). It showed that the thermal stability was not affected by the increment of styrene composition in the copolymer. Furthermore, by adding Fe_3O_4 in the copolymer, the thermogram showed only one step of weight loss from 130 to 430°C (Figure 6). This result is comparable with the previous study reported by Hao et al. (2011) that the copolymer with Fe_3O_4 has a higher thermal stability and does not easily decompose at a lower temperature.

The morphology of poly (GMA) and copolymers with Fe_3O_4 is presented in Figure 7. The copolymer beads

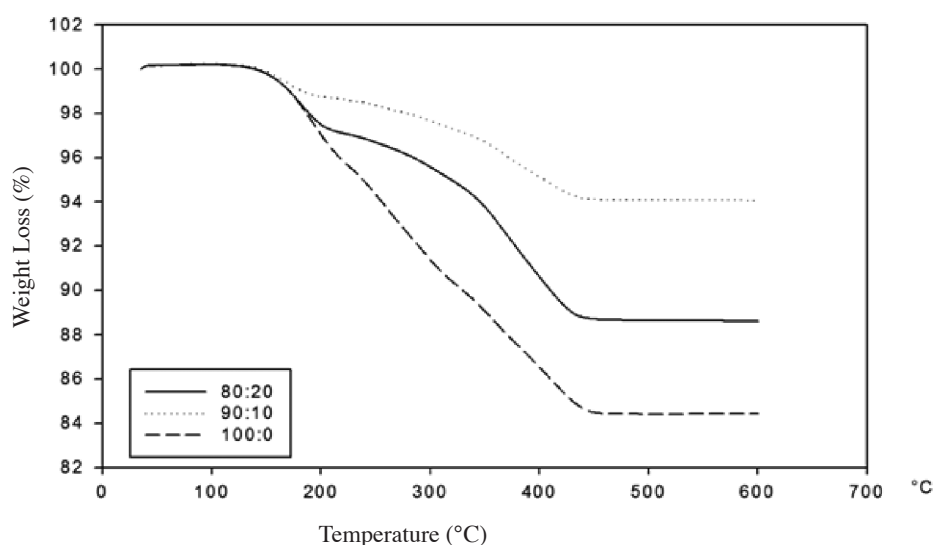


FIGURE 5. TGA thermograms for poly(GMA), poly(GS91) and poly(GS82)

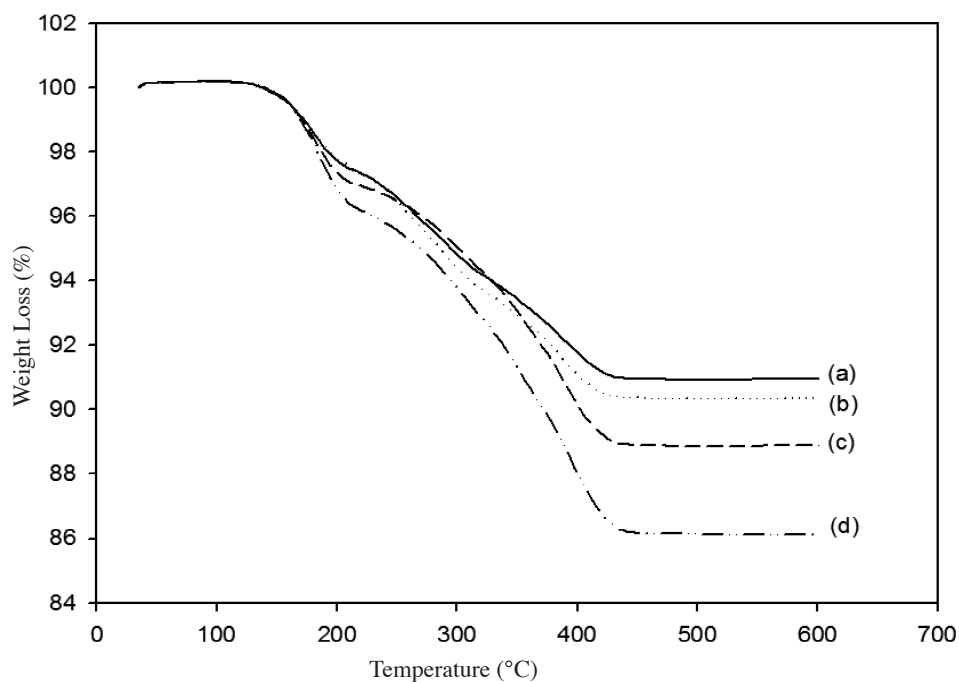


FIGURE 6. TGA thermograms for the copolymers containing Fe₃O₄ (a) GS 82/0.1% Fe₃O₄, (b) GS 82/0.2% Fe₃O₄, (c) GS 91/0.1% Fe₃O₄ and (d) GS 91/0.2% Fe₃O₄

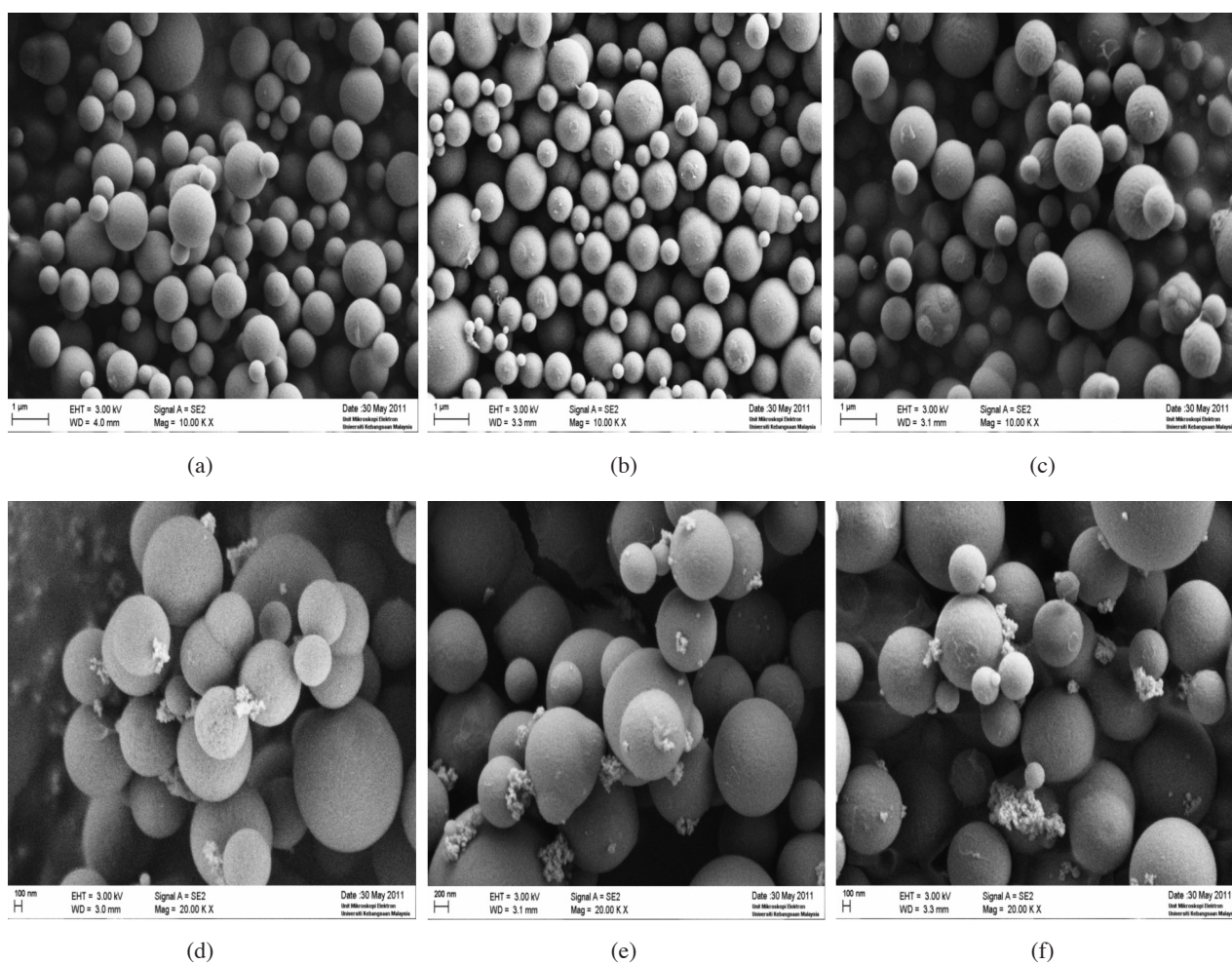


FIGURE 7. FESEM micrographs for (a) poly(GMA) (b) poly(GS91), (c) poly(GS82), (d) poly(GMA)/0.1% Fe₃O₄, (e) poly(GS82)/0.1% Fe₃O₄ and (f) poly(GS82)/0.2% Fe₃O₄

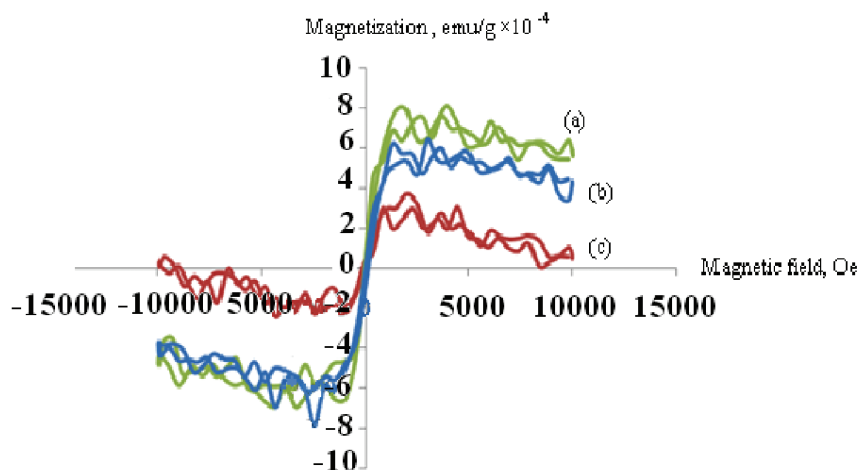


FIGURE 8. Magnetization curves for (a) poly(GS91)/0.2% Fe_3O_4 (b) poly(GS82)/0.3% Fe_3O_4 and (c) poly(GMA)/0.3% Fe_3O_4

formed non-uniform size of microspheres ranging from 0.5 to 1.5 μm . Besides that, the copolymers beads revealed a rough surface compared with poly(GMA), due to the presence of styrene and the roughness of the beads surface should be considered as a factor providing an increase in the surface area (Denizli et al. 2005). The same finding has been reported by Kuroda and Ozawa (1995). In addition, the micrographs showed that the Fe_3O_4 nanoparticles were entrapped within the polymer spheres.

One of the important parameters defined when discussing the magnetic materials using VSM is the amount of reversed magnetic field necessary to bring the flux density in the magnet to zero. This amount of magnetic field is defined as materials coercivity, H_c . High coercivity is a key measure in establishing a magnetic resistance to demagnetization. The results as shown in Figure 8 exhibited the copolymers have soft ferromagnetic properties that will have no remanent magnetization. Soft magnetic materials have the ability to be magnetized, then magnetized in the opposite direction with little energy loss in the hysteresis loop. In this study, the poly(GMA with 0.3% w/v Fe_3O_4) exhibited saturation magnetization (M_s) of $304 \times 10^{-6} \text{ emu g}^{-1}$, lower than poly(GS91) with 0.2% w/v Fe_3O_4 and GS82 with 0.3% w/v Fe_3O_4 . Besides that, the poly(GMA) with 0.3% w/v Fe_3O_4 possessed the highest coercivity (H_c) of 403.6 Oe compared with poly(GS91) with 0.2% w/v Fe_3O_4 and GS82 with 0.3% w/v Fe_3O_4 obtained 78.67 G and 48.29 Oe, respectively.

CONCLUSION

Magnetic polymer microspheres with various compositions of GMA and styrene were prepared by suspension photopolymerization. FTIR analysis proved that the C=C group in the aromatic ring from styrene was attached with GMA and after introduction of Fe_3O_4 , the absorption peaks corresponding to the vibration of Fe-O were also obtained. Poly(GMA-co-styrene) with Fe_3O_4 obtained higher thermal stability and formed microspheres from 0.5 to 1.5 μm .

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